

Transport and magnetic anomalies due to A-site ionic-size mismatch in $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$

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We present the results of electrical resistivity (ρ), magnetoresistance (MR) and dc and ac susceptibility (χ) measurements on polycrystalline samples of the type, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, synthesized under identical heat-treatment conditions. The substitution of larger Ba ions for Ca results in a *non-monotonic* variation of Curie temperature (T_C) as the system evolves from a charge-ordered insulating state for $x=0.0$ to a ferromagnetic metallic state for $x=0.5$. An intermediate composition, $x=0.1$, interestingly exhibits ferromagnetic, insulating behavior with thermal hysteresis in ac χ around Curie temperature ($T_C=120$ K). The $x=0.2$ and 0.3 compounds exhibit semi-conducting-like behavior as the temperature is lowered below 300 K, with a broad peak in ρ around 80-100 K; these compositions exhibit a weak increase in ρ as the temperature is lowered below 30 K, indicative of electron localisation effects; these compositions also undergo ferromagnetic transition below about 200 and 235 K respectively, though these are non-hysteretic; above all, for these compositions, MR is large and conveniently measurable over the entire temperature range of measurement below T_C and this experimental finding may be of interest from the applications point of view. We infer that the A-site ionic-size mismatch plays a crucial role in deciding these properties.

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The observation of large magnetoresistance (MR) in the vicinity of Curie temperature (T_C) in hole-doped LaMnO_3 systems, both in thin film as well as polycrystals,^{1,2} opened up a new direction of research, viz., giant magnetoresistance (see, for instance, Refs. 3-4). From the applications point of view, it is desirable⁵ to identify systems exhibiting conveniently measurable electrical resistivity (ρ) and a large MR over a wide temperature range. In this sense, the observation of such an effect in polycrystalline thin films as well as in bulk form (but not in epitaxial thin films and bulk single crystals) of $\text{La}_{2/3}(\text{Ba},\text{Ca})_{1/3}\text{MnO}_3$ is of considerable interest.⁵⁻⁷ Apparently, the presence of strains across the grain boundaries is an important deciding factor for such a behavior.⁶ In this respect, we considered it worthwhile to carry out investigations on the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, as there is a large lattice strain induced by size-mismatch between Ca and Ba. Our results reported here establish large magnetoresistance for $x= 0.2$ and 0.3 compositions over a wide temperature range as the temperature is lowered below T_C ; the magnitude of MR is precisely measurable down to 4.2 K considering that these compositions are not insulators at low temperatures in zero field.

There is also another motivation for the investigation of this Ba substituted series. It is known that the $x= 0.0$ oxide exhibits a charge ordered (CO) antiferromagnetic (AF) insulating state below 150 K and the ferromagnetism sets in below 220 K (see the articles cited in Ref. 8). The substitution of a bigger divalent cation, Sr^{2+} for Ca^{2+} , in the above series enhances the strength of double exchange (DE) interaction; this results in a gradual transformation of the insulating antiferromagnetic CO state into a DE ferromagnetic metal as the Sr concentration is increased resulting in a monotonic increase of T_C .⁸ While the magnetic and transport behavior sensitively depend on the size of A-site average ionic radius in general in these perovskites,⁹ there are few reports emphasizing the role of size-mismatch of the ions at the A-site on the properties.^{10,11} It is therefore of interest to explore how the properties are modified by a higher degree of lattice strain, which can be induced by substituting Ba for Ca considering a large variation in the average A-site radius from 1.198\AA to 1.343\AA for $x= 0.0$ and 0.5 respectively (while substituting Ba for Ca).

At this juncture, we would like to remark that there is very little work in the literature on the influence of Ba substitution for Ca in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. In fact, system-

atic studies on $\text{R}_{1-x}\text{Ba}_x\text{MnO}_3$ ($\text{R}=$ rare-earth) are also scarce, which prompted Barnabe et al¹² to investigate phase transitions and magnetoresistance in the $\text{R}= \text{La}$ series, though there are some reports on specific compositions close to $x= 0.3$ (Ref. 6, 7, 9, 13-17). It is also to be noted that the magnetic behavior of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is extremely sensitive to sample preparative conditions and impurities and that the magnetic phase diagram is very complex around $x= 0.5$ [See, for instance, 8, 18, 19, 20]. Therefore, it is absolutely essential to keep the starting materials and sample-preparative conditions the same for a series of compounds, if one has to compare the properties of several compositions within such a series. We have therefore taken sufficient care in the present investigation in this respect.

Polycrystalline samples of the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$ ($x= 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5), have been prepared by a standard solid state reaction route using required amounts of high purity (better than 99.9%) La_2O_3 , CaCO_3 , BaCO_3 and Mn_2O_3 with heat treatment similar to that mentioned in Ref. 19, except that the final sintering was done for 7 days. We have to necessarily perform final sintering for such a long duration, as otherwise the ferromagnetic transitions in these compounds are found to be spread over a wider temperature range. The x-ray diffraction patterns taken with Cu-K_α radiation are shown in Fig. 1; the positions of the diffraction lines and the lattice constants derived from these patterns (table 1) clearly highlight systematic lattice expansion with the substitution of Ba for Ca. The data were analysed by the Rietveld method using the program FULLPROF.²¹ We find that the samples are single phase for $x < 0.4$, forming in an orthorhombic structure with the space group Pnma (Ref. 22). For higher compositions there are additional weak lines which appears to arise from an extra phase, identified as BaMnO_3 (also see Ref. 20); it appears that, even for $x= 0.5$, we are able to retain orthorhombic structure in contrast to the cubic structure reported by Barnabe et al¹² and this discrepancy is attributed to different sample-preparative conditions. In fact, the value of the well-known "tolerance factor" ($t= [\text{r}_A + \text{r}_O]/\sqrt{2}[\text{r}_B + \text{r}_O]$, a measure of deviation of the ABO_3 perovskite structure from cubicity), listed in table 1 for all compositions, is 0.976, well below unity for this composition. Therefore, it is not unnatural that this composition is non-cubic. The ρ measurements were done by a four probe method in

the presence and the absence of a magnetic field (H) employing a conducting silver-paint for electrical contacts; the magnetoresistance ($MR = \Delta\rho/\rho = [\rho(H)-\rho(0)]/\rho(0)$) measurements were performed in the longitudinal mode. Dc magnetic susceptibility (χ) measurements ($H= 2000$ Oe and 100 Oe; zero-field-cooled (ZFC)) were performed employing a superconducting quantum interference device (SQUID) in the temperature range 4.2-350 K; the data for the field-cooled (FC) state of the specimens were also collected in the presence of $H= 100$ Oe; isothermal magnetization (M) measurements were performed at 4.2 K up to 55 kOe. Ac χ measurements (4.2-350 K), with a frequency of 105 Hz and a driving field of 0.8 Oe, were also performed both while cooling as well as warming the samples.

The results of ρ measurements are shown in Figs. 2 and 3. As known in the literature, $x= 0.0$ compound shows insulating behavior as a result of which the values of ρ below 50 K are not measurable; however, the application of H , say 30 kOe, results in a significant reduction of low temperature ρ due to the melting of the CO state (Fig. 3a). The same is qualitatively the case for $x= 0.1$ as well (see Fig. 3b). Further substitution of Ba results in gradual reduction of ρ (see Fig. 2), showing the transformation of the insulating ($x=0.0$) state to a metallic ($x=0.5$) phase. The intermediate compositions ($x= 0.2, 0.3,$ and 0.4) exhibit negative temperature coefficient of ρ (semiconducting-like) below 300 K followed by a broad hump at around 50, 100 and 200 K respectively; these humps possibly arise from grain boundary effects [6,7]. Thus, the resistivity values, though large, are in the convenient range of measurement down to 4.2 K even in zero-field, unlike $x= 0.0$ and 0.1 compounds. It is to be noted that, in the $x=0.2$ and 0.3 compounds, there is a weak increase in ρ at low temperatures ($T < 30$ K, see Fig. 3c). Recently, there have been reports [6,7] on A-site mismatch induced electron-localization in some of the rare earth manganites. The relevant parameter which characterizes this disorder is the variance (σ^2) (Ref. 17) of ionic radii at the A-site, and this parameter is rather large for $x= 0.2$ and 0.3 of Ba as compared to Sr doping (see table 1). Hence, disorder induced electron-localization effects may be operative in the Ba-substituted compounds. The application of magnetic field for these intermediate compositions depresses the magnitude of ρ at low temperatures and it must be emphasized that the magnitude of this depression is larger at temperatures far below respective T_C

values (see below). Clearly, the magnitude of (negative) MR is large and precisely measurable in the temperature range 4.2-100 K (-70 to -80%; see Fig. 3c, inset) for these compositions, unlike the situation in $x= 0.0$ and 0.1 . Following the arguments in Refs. 6 and 7, we attribute the low temperature enhancement of MR to size-mismatch effects across the grain boundaries. When measured as a function of H at 4.2 K, ρ undergoes a sharp drop for initial application of H due to the dominant scattering response across grain boundaries, followed by a slower fall with further increase of H (Fig. 3d). MR exhibits hysteretic behavior apparently due to such grain boundary effects in ferromagnets. For the compositions at the Ba rich end, which are metallic, there is no worthwhile feature in MR and hence we do not present these results here.

In order to understand the magnetism of these oxides better, we have performed magnetization studies as well. In the dc χ vs T data (Fig. 4), we find a sharp increase of χ for all the compositions below a certain temperature, attributable to the onset of ferromagnetic ordering. The value of T_C inferred from this rise (around 250, 120, 200, 235, 300 and 340 K for $x= 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) undergoes non-monotonous variation with Ba substitution. Even if the heat treatment is the same as that employed in Ref. 8, we see a similar trend, though these transitions are very broad for such short-time heat treatments. It may be recalled that, in the Sr-substituted samples [8], T_C monotonically increases with x , which is consistent with the well-known direct relationship between A-site ionic size and DE-mediated ferromagnetism. The breakdown of this relationship in the present series should arise from the strains in the lattice induced by initial Ba substitution. We therefore interpret the observed non-monotonic trends in T_C in the Ba substituted compounds in terms of a competition between the disorder-induced electron-localization and an enhancement of the DE-induced ferromagnetism resulting from an increase in the angle subtended by Mn-O-Mn bond and/or a decrease in the O2p covalent mixing strength with increasing Ba concentration.¹⁰ Similar non-monotonic variation of T_C due to size-mismatch effects has been known, to our knowledge, in only one system, viz., $Pr_{0.5}(Ba,Sr)_{0.5}MnO_3$ (Ref. 11) and, in this sense, our finding gains importance.

We note the following minor discrepancies in the observed values of T_C with those reported in the litera-

ture for the two end members. It is well known [8, 19] that the $x= 0$ compound orders ferromagnetically at 225 K; slightly higher T_C value for this composition in the present studies must be due to different heat-treatment conditions, as the starting raw materials are the same as those employed in Ref. 8. In the same way, our T_C value for $x= 0.5$ is larger than that reported (about 290 K) by Barnabe et al,¹² which could be attributed to cubicity of our sample as mentioned earlier. It may be added that, on the basis of investigations on $\text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$, Ju et al⁶ conclude that oxygen deficiency lowers the value of T_C and hence we believe that the oxygen non-stoichiometry (deviation from 3) is relatively less in our samples. For $x= 0.0$, we note that the drop in χ due to the onset of antiferromagnetism below 150 K (Ref. 8 and 19) is virtually absent, though the reduced magnitude of high-field magnetization (see below) is indicative of the existence of an antiferromagnetic component; presumably, the present sample preparative conditions induce canting in the spin structure inducing a ferromagnetic component for this composition even below about 150 K; this low temperature ferromagnetic component cannot be of DE-mediated type unlike the one setting in around 250 K, as otherwise one should have observed metallicity at low temperatures.

There are also other interesting features in the dc and ac magnetization data:

- As is well-known, ac χ shows (Fig. 5) hysteretic behavior while cooling and warming in the temperature range 75-140 K for $x= 0.0$ due to first-order nature of the charge-ordered antiferromagnetic transition.⁸ Interestingly, the same hysteretic behavior is seen for $x= 0.1$ as well around the temperature at which there is an onset of *ferromagnetic* ordering. It is not clear whether this signals the persistence of CO around 100 K for this composition as well (nearly at the same temperature as T_C !). In any case, our data seem to provide evidence for the first-order nature of the ferromagnetic transition similar to the observation on $\text{La}_{0.52}\text{Gd}_{0.15}\text{Ca}_{0.33}\text{MnO}_3$ (Ref. 23), a behavior not so common among the family of Mn-based perovskites.
- It is interesting to note that that the composition $x= 0.1$ is insulating and hence this sample is not

a DE-mediated ferromagnet. Thus this series provides an opportunity to traverse from spin-canted, charge-ordered, insulating state to a metallic, DE-ferromagnet via a (charge-ordered?) insulating ferromagnet by varying Ca/Ba ratio.

- The isothermal magnetization (M) (Fig. 6) rises sharply for initial applications of H (below 10 kOe) for all compositions. M saturates to a value close to $3.1 \mu_B$ for all compositions, except for $x= 0.0$, typical of that known for the ferromagnets of this class of Mn-perovskites; the values are however low (close to $1 \mu_B$) at high fields for $x= 0.0$, without saturation even at high fields; this observation attests our earlier remark that this alloy is essentially a canted antiferromagnet for the present sample preparative conditions. It is interesting to note that in the Sr doped compounds,⁸ the low temperature antiferromagnetic state is enhanced for initial Sr substitution (up to $x= 0.2$), whereas for Ba doping, $x= 0.1$ is sufficient to depress antiferromagnetism. If an antiferromagnetic interaction coexists with ferromagnetism for x (Ba)= 0.1, it may occur below 50 K as evidenced by a shoulder in ZFC dc and ac magnetization (see Fig. 4 and 5). However this component is suppressed/modifies by the presence of H or field cycling. Further observations made below render additional support to this view and the canted nature of low temperature magnetic structure.
- In the M versus H plots (Fig. 6), for $x= 0.0$ and 0.1, as the field is increased, there is a strong irreversibility between the initial magnetization while increasing the field and the one while decreasing the field, as shown in Fig. 6. These features are similar to those reported in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ (Ref. 24). For $x= 0.1$, we observe a more spectacular feature in the sense that, in the initial curve, there is a sudden increase in M at about 35 kOe. We attribute these features to possible small canting of magnetic structures, which is presumably altered by the application of H .
- The coercive field values are found to be typically 100 Oe for $x< 0.3$, beyond which the value is still closer to zero; these values suggest that the samples are soft ferromagnets. (vi) The ZFC and FC ($H=$

100 Oe) dc χ curves tend to deviate from each other from a lower temperature compared to respective T_C values, presumably due to the anisotropy of the materials (plots shown only for three compositions in Fig. 4b for the sake of clarity of the figure). Similar divergencies have been known even in other magnetic materials exhibiting long range magnetic ordering and hence need not be associated with spin-glass ordering.²⁵ The percentage of the divergence ultimately at low temperatures, however, decreases with the increase of Ba concentration, which we attribute to corresponding decrease of metastability.

Thus, we have traced the transformation of the CO insulating state ($x=0$) into a ferromagnetic-like metal ($x=0.5$) with increasing Ba concentration in $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, interestingly traversing through an insulating ferromagnetic compound with a non-monotonic variation of T_C with x . We made several interesting observations in the magnetic and transport behavior of these oxides. For $x=0.2$ and 0.3 , the magnetoresistance is quite large and precisely measurable over a wide temperature range well below T_C , an observation which may be of importance for applications. We would like to add that, at the time of writing this article, we came across a publication by Zhong et al²⁶ reporting the observation of a large MR over a wide temperature range in another manganite, $\text{La}_{0.55}\text{Dy}_{0.12}\text{Ca}_{0.33}\text{MnO}_3$, and thus there is a considerable interest in identifying systems with such properties. The results establish that the A-site ionic-size mismatches play a decisive role on the transport and magnetic behavior in these manganites.

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FIG. 1. X-ray diffraction patterns at 300 K of some compositions of the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. The asterisks for Ba rich compositions mark the lines arising from an extra phase, presumably due to BaMnO_3 . The pattern around the most intense lines are shown in an expanded form in the inset.

FIG. 2. Electrical resistivity (ρ) as a function of temperature for the compounds, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$.

FIG. 3. Temperature dependent electrical resistivity (ρ) behavior for $x= 0.0, 0.1, 0.2$ and 0.3 samples of the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$, in zero magnetic field and in a field of 30 kOe is shown in (a), (b) and (c). The temperature dependent magnetoresistance for $x= 0.2$ and 0.3 is shown in the inset of (c). ρ as a function of magnetic field (H) at 4.2 K for $x= 0.2$ and 0.3 is shown in (d).

FIG. 4. (a) Dc magnetic susceptibility (χ) as a function of temperature measured in a magnetic field of 2 kOe and (b) typical zero-field-cooled and field-cooled χ behavior measured in a field of 100 Oe, for the compounds, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$.

FIG. 5. Temperature dependent ac susceptibility behavior, for the compounds, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. For two compositions, $x= 0.0$ and 0.1 , we observe hysteresis behavior while cooling and warming (shown separately in the upper part of the figure).

FIG. 6. Isothermal magnetization behavior at 4.2 K for the series, $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$. The data for $x= 0.4$ is practically the same as that for $x= 0.5$. For $x= 0.0$ and 0.1 , the deviation of the field-cycled magnetization from the initial magnetization (that is, for increasing magnetic field) is shown in the insets.

TABLE I. Lattice parameters, average A-site ionic radius ($\langle r_A \rangle$), tolerance factor (t), variance (σ^2) of A-site ionic size and Curie temperature (T_C) in the $\text{La}_{0.5}\text{Ca}_{0.5-x}\text{Ba}_x\text{MnO}_3$ compounds. The σ^2 values for the Sr compounds are also given. The errors in the lattice parameters are estimated to be 0.004 Å.

x	a (Å)	b (Å)	c (Å)	$\langle r_A \rangle$	t	σ^2	Ba(Sr)	T_C (K)
0.0	5.413	7.631	5.424	1.198	0.923	0.0003 (0.0003)		250
0.1	5.437	7.655	5.461	1.227	0.933	0.0069 (0.0014)		120
0.2	5.487	7.713	5.501	1.256	0.944	0.0117 (0.0021)		200
0.3	5.480	7.731	5.509	1.270	0.954	0.0148 (0.0025)		235
0.4	5.499	7.759	5.511	1.285	0.965	0.0163 (0.0025)		300
0.5	5.522	7.793	5.533	1.314	0.976	0.0162 (0.0022)		340











